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The Morphology of Si-K-HAs Composite Prepared by Spray Drying

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Abstract. The silica potassium humic substance (Si-K-HAs) composite have been produced by spray drying successfully. In the previous studied the preparation of Si-K-HAs gel by precipitation method required the addition of acid so that Si-K-HAs gel product contains acid salts. This study was develope spray drying method in order to eliminate the use of acid. The mixture of potassium silicate, cellulose, and humic potassium solution was mixed with varying volume ratios and flowed into a spray dryer to produce Si-K-HAs powder. The used of cellulose (CMC) in this study acts as a homogeneous agent so that silica and humic substance can be completely mixed at controlled viscosity. Si-K-HAs products were characterized by Scanning electron microscopy (SEM), X-ray fluorescence (XRF), X-ray diffraction (XRD), Fourier transform infrared spectrometry (FTIR), and Surface area analytical (SAA). The result showed that the Si-K-HAs composite prepared by spray dryers have spherical particles, SiO_2 in the range of 48-50%, K_2O in the range of 49-50%. The presence of cellulose caused the increasing of Si-K-HAs particle size from 17.30 μm (prepared without CMC) to 41.11 μm (prepared with the addition of 100g of CMC). The presence of cellulose can also increase the surface area of the spray-dried Si-K-HAs particles from 111.92 m^2g^{-1} to 163.241 m^2g^{-1}.

Introduction

Silica composite and silica hybrid have been developed with several methods for a wide variety of applications [1-3]. The production of silica-potassium-humic substance composites (Si-K-HAs) from potassium silicate and potassium humate solution by precipitation method using acid both gradually [4] and simultaneously [5] have been investigated in the previous studies. The effect of acid types on the characteristics of Si-K-HAs has also been studied [5]. Si-K-HAs composite is a new material developed to support the agricultural sector, especially for the manufacture of silica base fertilizer. The formation of Si-K-HAs gel by precipitation method was needed the acid or acid salt for reduction of acidity level (pH) of the alkaline solution. To avoid the use of acids for the manufacture of Si-K-HAs composites, Si-K-HAs solidification method was developed using spray dryers in the absence and the presence of cellulose.

Spray drying is a method for producing strong particles in its application in several industries, among others in the food, beverage, chemical, pharmaceutical and ceramics industries [6,7]. This method allows fast and continuous particle production within a reasonable size range where polydisperse droplet growth undergoes diverse trajectories and drying which culminates in the reproducibility of the particle properties and functionality. The spray dryer nozzle also affects monodisperse droplets. These monodispersed droplets pass through a single-flow drying chamber where they come into contact with hot air to produce particles that are diverse or uniform in size, shape, and properties [8]. Ide et al [9] reported that two other factors affecting morphology are gas flow rate and the ratio of H_2O to raw material (TEOS), which both have a positive effect on morphology. The study demonstrated that drying nanocapsules using silica as the auxiliary agent by spray drying process enables the obtaining of dried micronic particle size. For the higher heatsensitive product like silica, the residence time is the very important factor but this cannot only affect to the particle degradation because in the spray dryer there may be the occurrence of very hot and cold zones [10].

The purpose of this study was to produce silica-potassium-humic-substances (Si-K-HAs) composite particles using spray dryer with and without the addition of cellulose. In an addition, the use of the spray dryer method is in order to avoid the use of acid needed in the precipitation method as has been done in previous studies. The cellulose in this study comes from carboxyl methyl cellulose (CMC) which will act as a homogeneous agent so that silicate and humic substances solution can be completely mixed in the controlled viscosity. The effect of the initial concentration of silica and gram of CMC (cellulose) in the Si-K-HAs solution on morphologies and characterization of Si-K-HAs particles was investigated with scanning electron microscopy (SEM), surface area (SAA-BET), IR-spectra, X-ray diffraction, and X-ray fluorescences.

Materials and Methods

Materials. Geothermal sludge (91% SiO_2) as silica source was obtained from the geothermal plant in Dieng Wonosobo Indonesia. Peats was obtained from Banjarmasin Kalimantan Indonesia as a source of humic substance. Carboxyl methyl cellulose (CMC) as cellulose source and potassium hydroxide as a solvent was obtained from chemical distributor CV Medica Vanjaya. All the reagents purchased commercially and used without purification.

Spray Dryer. Spray dryer apparatus have vaporation capacity 4 L/h water, Sample volume 2 L – 8 L, Drying air flow rate up to 55 m^3/h, Spray flow rate 1 – 5 L/h, Heating power 2500 W Max. inlet temperature 120 °C, Chamber size (D, H) 85 cm, 160 cm, Typical yield 40 – 60%, Particle size 2 – 50 µm.

The preparation of silicate-potassium-humic solution. Both geothermal sludge and peat reduce in size by mill until reach 100 mesh. Geothermal sludge powder (500g) and peat powder (300g) was extraction using potassium hydroxide solution 5L (3N) in reactor stirred tank respectively to produced potassium silicate and potassium humate. Potassium silicate and potassium humate solution were mixed in the volume ratio of 1:1 and 1:2 to reach a 4L mixed solution. The cellulose (CMC) was added to the solution of 30; 100; 200 g then mixing to reach the homogeny solution. The solutions have the viscosity in the range of 16-18 °Be then flowing to the top of the spray dryer.

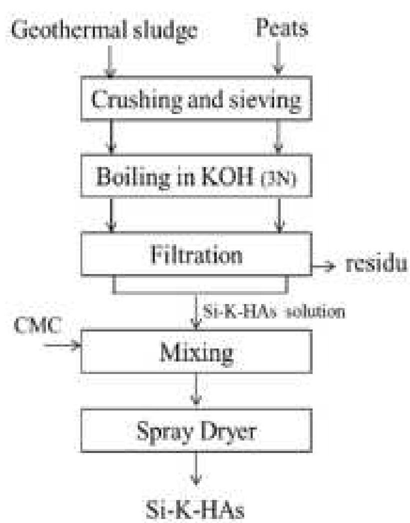


Fig. 1. Flow diagram of Si-K-HAs production.

Characterization. Scanning electron microscopy (SEM) was used to observe the morphology of the samples.The composition of Si-K-HAs was analyzed by energy dispersive X-ray fluorescence spectrometry (EDXRF, Minipal 4, PANalytical). X-ray diffraction patterns of the samples were obtained using an X-ray diffractometer (X'pert, Philips). The surface area (multi-point BET) were obtained using Quantachrome NovaWin and IR-spectra of the samples were analyzed using Fourier transform infrared spectroscopy (FTIR).

Results and Discussion

Table 1 showed the composition of Si-K-HAs powder from spray dryer. Si-K-HAs product prepared by Si-K-HAs solution without the presence of cellulose has a composition of 51% SiO_2 and 48.9% K_2O. The celluose (CMC) was added into Si-K-HAs solution from 30 to 200 g indicated no significant change on composition e.g. about 48.3 to 48.9 % SiO_2 and K_2O about 50.2 to 50.9% respectively. The composition of humic substance in Si-K-HAs product was indicated by IR spectra as shown in Fig. 2.

Table 1. Composition of Si-K-HAs.

CMC [g]	SiO_2 [%]	K_2O [%]
without CMC	51.0	48.9
30 CMC	48.9	50.9
100 CMC	49.1	50.7
200 CMC	48.3	50.2

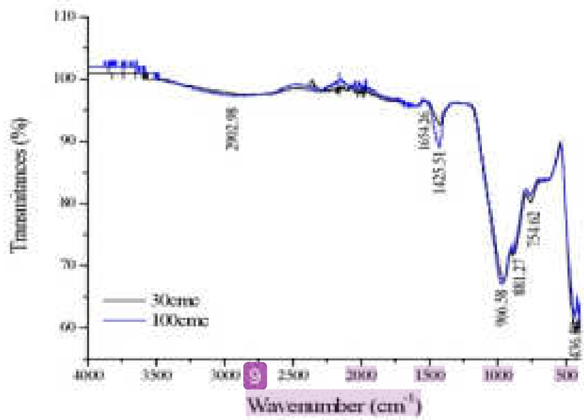


Fig. 2. IR spectra of spray dried Si-K-HAs.

The IR spectra for silica gel was characterized by the presence of silanol hydroxyl groups and also the molecules adsorbed on the oxide surface through hydrogen bonds usually appear quite sharp in the region of about 3400 cm^{-1}. The IR spectrum of Si-K-HAs from the spray dryer as shown in Fig. 2 showed low intensity in the region of 3400 cm^{-1}. Characteristics of stretching of silane group (Si-OH) at 2902 cm^{-1} there was a low in intensity for Si-K-HAs particles which are probably caused by cellulose and humic substance. Bands at wave numbers 1654 and 966 cm^{-1} associated with SiO-H bending and Si-OH bending respectively, while at 881 and 436 cm^{-1} are associated with SiO-H symmetrical stretching and Si-O bending vibration, respectively. The C=O bands in the wavenumber 1654 cm^{-1} were associated with carboxyl group deformation. The band at 1375 and 1425 cm^{-1} were indicated the CH_2.OH, and CHOH group respectively. The siloxane (Si-O-Si) groups are generally quite sharply appeared in the region of 1000-1100 cm^{-1}. The peak of about

966 cm^{-1}, which corresponds to the vibration of the Si-OH bond stretched explained by the presence of bound surface OH groups to Si.

Fig. 3 showed the SEM image Si-K-HAs powder from spray dryer prepared by a) without CMC b) added 30g CMC and c) added 100g CMC in the raw solution volume ratio of 1:1. SEM image of spray-dried silica-potassium mesoporous showed micro-sized spherical morphology. At the same magnification can be identified for the Si-K-Has prepared without CMC obtained the smallest particle diameter about of 3.46 µm, medium size 9.48 µm, and the largest particle diameter of 17.30 µm. The addition of CMC of 30g obtained Si-K-Has particles with the smallest diameter of 3.80, the medium size of 15.29 and the largest diameter of 26.47 µm. The addition of 100g of CMC obtained the smallest diameter of 5.64 µm medium size diameter 14.31 µm and the largest diameter at 41.11 µm. The Si-K-HAs sample prepared from sodium silicate with an additional 100 g of CMC (Fig. 2c) shows the presence of a ball sac containing silica particles in it. Aside from the ball pouch, there was also a sheet that looked like a soft torn cloth that might have come from the presence of cellulose.

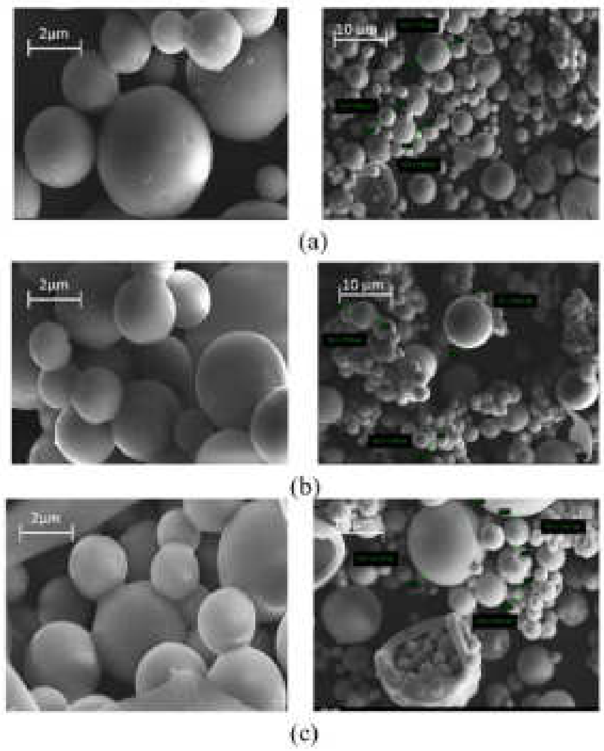


Fig. 3. SEM images Si-K-HAs particles prepared by (a) without CMC, (b) added 30 CMC and (c) added 100 CMC.

Fig. 4 showed the particles distribution of Si-K-HAs by Image-G method from SEM image. The addition of CMC from 30 to 100g showed the increase in particle size from the sample without CMC ie the smallest particle size increases from 3.45 to 5.64 µm, the middle size increases from 9.48 to 14.31 µm and the largest particle size increases from 17.30 to 41.11 µm. The addition of cellulose which was more than 200g CMC caused the solution to become more viscous so that the spray and drying process was disrupted and caused the product out of the dryer chamber resembles sludge and has not dried yet.

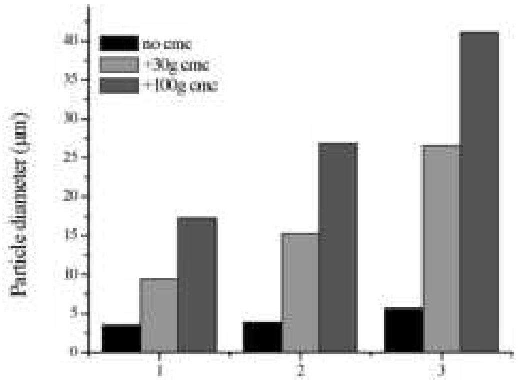
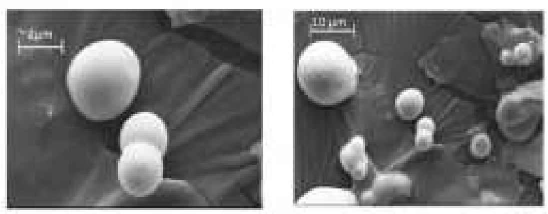
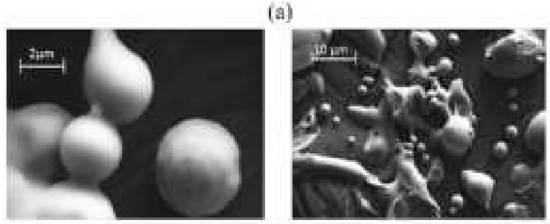


Fig. 4. Distribution of Si-K-HAs particles size prepared by Si-K-HAs solution at (a) the absence of CMC (b) added 30g CMC and (c) added 100g CMC.

Fig. 5 showed the SEM image for Si-K-Has particles produced from a raw solution where the ratio of potassium silicate to potassium humate was 1: 2 with the addition of a) 100g CMC and b) 200g of CMC on raw solution.



(a)



(b)

Fig. 5. SEM image of Si-K-HAs particles prepared by ratio raw solution of 1:2 with the addition of (a) 100g CMC and (b) 200g CMC.

The silica composite materials generated from a viscous-based dipotassium silicate humate complex in the presence of cellulose. The use of the silica-potassium-humate solution with a volume ratio of 1: 2 where potassium humate solution twice as much as potassium silicate solution shows different product morphologies with the use of a solution with a volume ratio of 1: 1. It was well known that humic compounds contain a lot of carbon. The SEM image in Fig. 5 showed a heterogeneous structure with ball-like silica particles embedded in a fine carbon matrix.

The results of the analysis for the surface area using SAA-BET for Si-K-HAs in absence of cellulose added 30g CMC and added 100 g CMC obtained surface area of 111.92 m^2g^{-1}; 163.241 m^2g^{-1} and 134.78 m^2g^{-1} respectively. This explained that the presence of cellulose can also increase the surface area of the spray-dried Si-K-HAs particles.

Powder X-ray diffraction pattern as shown in Fig. 6 indicated that Si-K-HAs solid dispersion particles were in amorphous structure.

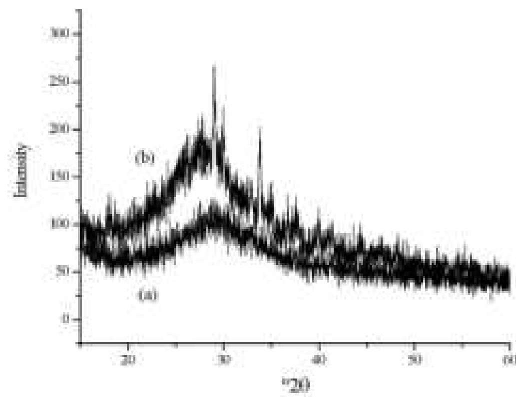


Fig. 6. Diffraction pattern of Si-K-HAs prepared by (a) 30 g CMC and (b) 100g CMC.

Summary

The silica-potassium-humic substance (Si-K-HAs) composite could be produced by spray drying successfully. The presence of cellulose (CMC) caused the increase of particle size until the additional of 100g CMC. The presence of cellulose can also increase the surface area of the spray-dried Si-K-HAs particles. The surface area of SI-K-HAs spray dried without CMC reach 111 m^2g^{-1} while the surface area with 30g and 100g CMC reached 163.241 m^2g^{-1} and 134.78 m^2g^{-1} respectively

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